J. Phys. Chem. A **2001,** *105,* 10393−10396

Separation of the Electric Polarization into Fast and Slow Components: A Comparison of Two Partition Schemes

M. A. Aguilar

Departamento de Química Física, Universidad de Extremadura, Avda. de Elvas s/n, 06071 Badajoz, Spain

Received: April 26, 2001; In Final Form: June 6, 2001

The study of nonequilibrium solvation with a dielectric continuum model requires splitting the electric polarization into two terms characterized by different relaxation times. There exist various schemes to perform this partition. We show that contrary to what had previously been indicated, the two most commonly used partition schemes, Pekar and Brady and Carr, yield the same value for the total reaction field and for the nonequilibrium free energy whenever one assumes a linear response regime. The confusion appears because in the older Pekar partition the part of the fast polarization in equilibrium with the nuclear polarization is included in the slow component.

Introduction

The use of dielectric continuum models in the study of electron transitions or charge-transfer processes has a long history. A classic description, in terms of dielectric constants, of the solvatochromic shift was first given by Lippert,[1] Ooshika,[2] Bayliss,[3] and McRae.[3,4] These authors consider a classic dipole inside a spherical cavity immersed in a continuum dielectric. Later developments have included the consideration of higher multipole moments[5] or of cavities of arbitrary symmetry.[6] In recent years, models that combine a quantum description of the solute with a classical description of the solvent in terms of dielectric models have also been widely used.[5−10] The main advantage of these models is that, because of their simplicity, they permit one to perform quantum mechanical self-consistent field (SCF) molecular orbital calculations for molecules in solution in exactly the same way as for molecules in vacuo or in the gas phase.

The fast movement of the electrons of the solute that occurs during an electron transition requires a dynamical treatment of solvation. It is then convenient to split the solvent polarization into two terms characterized by very different relaxation times. One component, associated with the movement of the solvent electrons, is considered to always be in equilibrium with the solute charge distribution. The other, associated with the movement of the solute nucleus, remains fixed during electron transitions. The faster component is usually referred to as electronic, optical, or noninertial polarization, while the slow component is known as nuclear, inertial, or orientational polarization. Although more general partitions[7] have been proposed, this division of the dielectric polarization into two components is in general enough to obtain an adequate description of the phenomena of electron transition.

Despite their widespread use, the scheme to follow in the division of the polarization into different contributions is not clear. In fact, as remarked by Klamt[8] or Cossi and Barone,[7] different approaches leading to different physical pictures exist and are still used. Most of the initial work on solvatochromic shift was based on the so-called Pekar partition. As is well-known, in equilibrium solvation the total response of the dielectric (inertial plus noninertial components) to the field generated by a dipole inside a spherical cavity is given as a function of the reaction field factor, $g(\epsilon)$, that, in the Onsager[11] model, takes the form

$$g(\epsilon) = \frac{2(\epsilon - 1)}{2\epsilon + 1}\frac{1}{a^3} \tag{1}$$

where ϵ is the static dielectric constant and a is the radius of the cavity that contains the solute molecule. In the Pekar partition one supposes that the electronic component of the reaction field is related to $g(\epsilon_{\mathrm{opt}})$, where ϵ_{opt} is the dielectric constant at optical frequencies, which is related to n^2, the square of the refraction index, $\epsilon_{\mathrm{opt}} = n^2$. The inertial component is then calculated as the difference between the total and the optical response. Brady and Carr[12] criticize this model and propose a new partition in which it is the total solvent dielectric susceptibility, $\chi = (\epsilon - 1)/4\pi$, and hence the polarization that is split into two terms $\chi = \chi_{\mathrm{fast}} + \chi_{\mathrm{slow}}$ where $\chi_{\mathrm{fast}} = (n^2 - 1)/4\pi$ and $\chi_{\mathrm{slow}} = (\epsilon - n^2)/4\pi$. A detailed description of this partition and its use in the study of solvatochromic shifts can be found in Aguilar et al.,[6] Klamt,[8] and more recently, Cossi and Barone.[7]

The aim of this present paper is to show that, when correctly used, the two partitions are equivalent and yield the same value of the experimental observables. We first will show that, assuming as valid a linear response regime, the two models provide exactly the same total reaction field, although obviously they predict different values for the fast and slow components. The differences between the two models appears because the Pekar partition includes in the slow component not only the contribution due to the nucleus movement but also the part of the electron component that is in equilibrium with the nuclear polarization. Next, we will study the solvatochromic shift. Also in this case the two models predict the same value. The confusion appears when one tries to use a determined partition with an unsuitable free energy expression. Each partition has to be used with a different expression for the nonequilibrium free energy. For the sake of clarity, we will limit the discussion to the case of a dipole in a spherical cavity, although the conclusions can be easily extended to the case of higher multipoles moments.

10.1021/jp011598f CCC: $20.00

The Reaction Field

We begin by defining our model. We assume a point dipole, $\vec{\mu}_0$, inside a spherical cavity of radius a surrounded by a continuum dielectric characterized by the value of the static dielectric constant, ϵ, and the square of the refractive index, n. As a consequence of the electron transition, the dipole moment changes from $\vec{\mu}_0$ to $\vec{\mu}$. We assume that the electronic (fast) part of the dielectric polarization is able to adjust instantaneously to the excitation. On the contrary, the inertial (slow) part has to be kept fixed during the electron transition and hence is in equilibrium with the value of the dipole moment of the solute in the ground state.

The Onsager reaction field in the ground state is $\vec{R}_0 = g(\epsilon)\vec{\mu}_0$. The Pekar partition calculates the contribution of the slow component as the difference between the responses of the dielectric when this is characterized by the dielectric constant or by the refractive index, $\vec{R}_{\mathrm{slow}} = [g(\epsilon) - g(n^2)]\vec{\mu}_0$. The fast component is assumed to be in equilibrium with the solute charge distribution in the excited state $\vec{R}_{\mathrm{fast}} = g(n^2)\vec{\mu}$. Hence, the total reaction field in the excited state just after the transition is

$$\vec{R} = \vec{R}_{\mathrm{slow}} + \vec{R}_{\mathrm{fast}} = [g(\epsilon) - g(n^2)]\vec{\mu}_0 + g(n^2)\,\vec{\mu} \qquad (2)$$

The Brady and Carr[12] partition splits the polarization vector into two terms. In the ground state the ratio between the slow and the total components is $P_{\mathrm{slow}}/P = \chi_{\mathrm{slow}}/\chi = (\epsilon - n^2)/(\epsilon - 1)$. The same relationship holds for charges induced on the cavity surface and hence for the reaction field

$$\vec{R}_{\mathrm{slow}} = \frac{\epsilon - n^2}{\epsilon - 1}\vec{R}_0 = \frac{\epsilon - n^2}{\epsilon - 1}g(\epsilon)\vec{\mu}_0 = \frac{2(\epsilon - n^2)}{2\epsilon + 1}\,\frac{1}{a^3}\vec{\mu}_0 \qquad (3)$$

As one can see, the value of the slow component of the reaction field differs clearly from the value obtained with the Pekar partition. For instance, if one takes a dielectric with $\epsilon = 78$ and $n^2 = 2$, the Pekar partition yields to a value of 0.58 $\vec{\mu}_0/a^3$ while the Brady and Carr partition yields 0.97 $\vec{\mu}_0/a^3$.

To obtain the contribution of the fast component and the total reaction field in the excited state just after the electron transition, we have to solve Laplace's equation by assuming that the dielectric response is characterized by the refractive index and that in the cavity surface we already have a charge distribution, σ_{slow}, due to the slow component of the polarization. The boundary condition that the system has to verify is[13b]

$$n^2\left(\frac{\partial V_1}{\partial r}\right) = \left(\frac{\partial V_2}{\partial r}\right) - 4\pi\sigma_{\mathrm{slow}} \qquad (4)$$

where V_1 and V_2 are the electrostatic potential outside and inside the sphere, respectively.

Aguilar et al.[6] give the solution to this problem for the case of the reaction potential of an arbitrary charge distribution and a spherical cavity:

$$V_{\mathrm{fast}}(r) = -\sum_l\sum_m\left[\frac{(l+1)(1-n^2)}{l+n^2(l+1)}E_l^m(\rho) - \frac{(l+1)^2(1-n^2)(\epsilon-n^2)}{[l+n^2(l+1)]\,[l+\epsilon(l+1)]}E_l^m(\rho_0)\right]\frac{r^n}{a^{2l+1}}P_l^m(\cos\vartheta)\mathrm{e}^{\mathrm{i}m\varphi} \qquad (5)$$

where $E_l^m(\rho) = (l - |m|)!/(l + |m|)!\int\rho(r)\, r^n P_l^m(\cos\,\vartheta)\mathrm{e}^{-\mathrm{i}m\varphi}\,\mathrm{d}r^3$ are the multipole moments that represent the solute charge distribution. For the case of a dipole $l = 1$, and given that $\vec{R}(r) = -\overrightarrow{\mathrm{grad}}\ V(r)$, we obtain

$$\vec{R}_{\mathrm{fast}} = g(n^2)\vec{\mu} + \frac{2(n^2-1)}{2n^2+1}\vec{R}_{\mathrm{slow}} = g(n^2)\vec{\mu} + \frac{4(n^2-1)(\epsilon-n^2)}{(2n^2+1)(2\epsilon+1)}\,\frac{1}{a^3}\vec{\mu}_0 \qquad (6)$$

One sees that, in this model, there exist two contributions to the fast component: The first is the response of the electrons of the dielectric to the solute charge distribution, and the second is the response to the surface charge originated by the slow component of the electric polarization. It is in this last term where the two models, Pekar and Brady and Carr, differ. In the Pekar model, the part of the fast polarization in equilibrium with the nuclear polarization, the last term in eq 6, is considered to be a part of the slow response. We denote this term as $\vec{R}_{\mathrm{fast(s)}}$. For the dielectric taken as example (ϵ =78 and $n^2 = 2$) the value of this term is not negligible: $\vec{R}_{\mathrm{fast(s)}} = 0.39\ \vec{\mu}_0/a^3$

In a linear response model, the two terms in eq 6 are independent of each other; i.e., $\vec{R}_{\mathrm{fast(s)}}$ is not affected by the change in the solute charge distribution that follows the transition, and hence its value is the same in the ground and excited states. Because of this, the two models yield the same value for the reaction field. In fact, if we add (3) and (6) and rearrange the terms, we obtain the prediction of the Brady and Carr partition for the total reaction field in the excited state:

$$\vec{R} = g(n^2)\vec{\mu} + \frac{6(\epsilon - n^2)}{(2\epsilon+1)(2n^2+1)}\,\frac{1}{a^3}\mu_0 = g(n^2)\vec{\mu} + [g(\epsilon) - g(n^2)]\vec{\mu}_0 \qquad (7)$$

which, as one sees, coincides with the value predicted by the Pekar model, eq 2. In summary, the two models yield the same value for the reaction field. The confusion appears because they use the same words, slow and fast, for contributions that are different.

Free Energy

To obtain the solvatochromic shift, it is necessary to calculate the difference between the free energies of the ground and excited states. In the ground state the dielectric is in an equilibrium situation. It is not necessary to split the polarization into its components and the solvation free energy is simply $-{}^1/{}_2 g(\epsilon)\vec{\mu}_0{}^2$. On the contrary, in the excited state it is a nonequilibrium situation. This problem was solved by Marcus[13] for the related problem of electron-transfer reactions. We shall use here the expressions proposed by Aguilar et al.[6] for the case of a solute in a cavity of arbitrary shape. The following expression was deduced by using the Brady and Carr partition and hence is only valid for this particular case

$$\Delta G = \frac{1}{2}\int V(r)\,\rho(r)\,\mathrm{d}r^3 - \frac{1}{2}\int V_{\mathrm{slow}}(r)[\rho_0(r) - \rho(r)]\,\mathrm{d}r^3 - \frac{1}{2}\int V_{\mathrm{slow}}[\sigma_{\mathrm{fast,0}} - \sigma_{\mathrm{fast}}]\,\mathrm{d}r^2 \qquad (8)$$

Here, $V(r)$ is the total reaction potential in the excited state characterized by a solute charge distribution, ρ, $V_{\mathrm{slow}}(r)$ is the slow component of the reaction potential, which is calculated in equilibrium with the solute charge distribution of the ground state, ρ_0, and $\sigma_{\mathrm{fast,0}}$ and σ_{fast} are the surface charges associated to the fast component of the polarization in the ground and excited states, respectively.

For the case of a dipole in a spherical cavity, we obtain the following values for the different integrals (see Appendix):

$$\frac{1}{2}\int V(r)\,\rho(r)\,\mathrm{d}r^3 = -\frac{1}{2}g(\epsilon)\vec{\mu}^2 - \frac{1}{2}[g(\epsilon) - g(n^2)]\vec{\mu}\vec{\mu}_0 \quad (9)$$

$$-\frac{1}{2}\int V_{\mathrm{slow}}(r)[\rho_0(r) - \rho(r)]\,\mathrm{d}r^3 = \frac{1}{2}\,\frac{2(\epsilon - n^2)}{(2\epsilon + 1)}\,\frac{1}{a^3}\vec{\mu}_0^{\,2} - \frac{1}{2}\,\frac{2(\epsilon - n^2)}{(2\epsilon + 1)}\,\frac{1}{a^3}\vec{\mu}_0\vec{\mu} \quad (10)$$

$$-\frac{1}{2}\int V_{\mathrm{slow}}[\sigma_{\mathrm{fast},0} - \sigma_{\mathrm{fast}}]\,\mathrm{d}r^2 = -\frac{1}{2}\,\frac{2(\epsilon - n^2)}{2\epsilon + 1}g(n^2)\vec{\mu}_0(\vec{\mu}_0 - \vec{\mu}) \quad (11)$$

Summing these three terms gives the final expression for the free energy of the excited state just after the electron transition:

$$\Delta G = -\frac{1}{2}g(\epsilon)\vec{\mu}^2 + \frac{1}{2}[g(\epsilon) - g(n^2)](\vec{\mu} - \vec{\mu}_0)^2 \quad (12)$$

The second term on the right-hand side (rhs) is usually known as the reorganization energy.[14]

In the case of the Pekar partition and due to the different meaning of the terms V_{slow}, $\sigma_{\mathrm{fast},0}$, and σ_{fast}, eq 8 cannot be used. In this case, and in order to obtain an expression for the nonequilibrium free energy, we shall follow Newton and Friedman,[15] who define a reversible path connecting the ground and excited states:

$$\Delta G = -\frac{1}{2}g(\epsilon)\vec{\mu}_0^{\,2} - \int_0^1(\vec{\mu} - \vec{\mu}_0)\vec{R}(\theta)\,\mathrm{d}\theta \quad (13)$$

where at an intermediate stage in the charging process, one has

$$\vec{\mu}(\theta) = \vec{\mu}_0 + \theta(\vec{\mu} - \vec{\mu}_0) \quad (14)$$

and

$$\vec{R}(\theta) = g(\epsilon)\vec{\mu}_0 + g(n^2)\theta(\vec{\mu} - \vec{\mu}_0) \quad (15)$$

When $\theta = 0$, we obtain the reaction field of the ground state and, when $\theta = 1$, the reaction field of the excited state, eq 2.

Substituting eq 15 into eq 13, we obtain

$$\Delta G = -\frac{1}{2}g(\epsilon)\vec{\mu}_0 - g(\epsilon)\vec{\mu}_0(\vec{\mu} - \vec{\mu}_0) - \frac{1}{2}g(n^2)(\vec{\mu} - \vec{\mu}_0)^2 \quad (16)$$

If we add and subtract from this expression the term $^1/_2 g(\epsilon)\vec{\mu}^2$ and we rearrange terms, we obtain

$$\Delta G = -\frac{1}{2}g(\epsilon)\vec{\mu}^2 + \frac{1}{2}[g(\epsilon) - g(n^2)](\vec{\mu} - \vec{\mu}_0)^2 \quad (17)$$

which is identical to eq 12.

Summary and Discussion

We have compared two different schemes for the separation of the electric polarization of a dielectric into two components, one associated with the slow response and the other with the fast response. The first scheme, known as the Pekar partition, is based on the separation of the reaction field into one component associated with the dielectric constant and another to the square of the refractive index. The second scheme also splits the dielectric susceptibility into two terms but yields expressions for the two components of the reaction field that differ from those obtained with the Pekar partition.

Two types of mistake are common. The first is to use the Pekar partition to obtain the slow component but the condition contour given by eq 4 to obtain the fast component. This procedure is not correct. In the Pekar partition the fast component is calculated as the response of the dielectric in equilibrium only with the solute charge distribution but never with the surface charge associated with the slow component. The consequence of this mistake is that the $\vec{R}_{\mathrm{fast(s)}}$ term is included twice.

The second type of mistake is to use the Pekar partition together with the free energy expression given by eq 8. The meaning (and magnitude) of the terms slow and fast in eq 8 is different from that in the Pekar partition. This confusion of terminology can lead to incorrect values of the solvatochromic shift (an example of the numerical errors associated with this mistake can be found in ref 7, where the authors compare the values obtained by using the same expression for the free energy but two different partition schemes).

In sum, when properly used, both partition schemes provide exactly the same value for the total reaction field and for the nonequilibrium free energy, but only if the dielectric response is linear. The equivalence between the two models breaks down when the dielectric behavior is nonlinear. For the nonlinear regime one of the assumptions of the Pekar partition (that the value of the term $R_{\mathrm{fast(s)}}$ is independent of the solute charge distribution) is not valid and hence the Pekar model can yield incorrect results. In this case the use of the Brady and Carr partition is compulsory.

Appendix: Nonequilibrium Free Energy

The first integral is immediate

$$\frac{1}{2}\int V(r)\,\rho(r)\,\mathrm{d}r^3 = -\frac{1}{2}\sum_m\frac{2(n^2 - 1)}{(2n^2 + 1)}\,\frac{\mu_m}{a^3}\int rP_1^m(\cos\theta)\mathrm{e}^{\mathrm{i}m\varphi}\rho\,\mathrm{d}r^3 - \frac{6(\epsilon - n^2)}{(2\epsilon + 1)(2n^2 + 1)}\sum_m\frac{\mu_{0,m}}{a^3}\int rP_1^m(\cos\theta)\mathrm{e}^{\mathrm{i}m\varphi}\rho\,\mathrm{d}r^3 = -\frac{1}{2}g(\epsilon)\vec{\mu}^2 - \frac{1}{2}[g(\epsilon) - g(n^2)]\vec{\mu}\vec{\mu}_0 \quad (18)$$

For the second integral we have

$$-\frac{1}{2}\int V_{\mathrm{slow}}(r)[\rho_0(r) - \rho(r)]\,\mathrm{d}r^3 = \frac{1}{2}\,\frac{2(\epsilon - n^2)}{(2\epsilon + 1)}\sum_m\frac{\mu_{0,m}}{a^3}\int rP_1^m(\cos\vartheta)\mathrm{e}^{\mathrm{i}m\varphi}(\rho_0 - \rho)\,\mathrm{d}r^3 = \frac{1}{2}\,\frac{2(\epsilon - n^2)}{(2\epsilon + 1)}\,\frac{1}{a^3}\vec{\mu}_0(\vec{\mu}_0 - \vec{\mu}) \quad (19)$$

To solve the third integral, it is convenient to perform the following transformation

$$-\frac{1}{2}\int V_{\mathrm{slow}}[\sigma_{\mathrm{fast},0}-\sigma_{\mathrm{fast}}]\,\mathrm{d}r^2 = -\frac{1}{2}\int \sigma_{\mathrm{slow}}(V_{\mathrm{fast},0}-V_{\mathrm{fast}})\,\mathrm{d}r^2 \quad (20)$$

where σ_{slow} is

$$\sigma_{\mathrm{slow}}(r) = -\frac{6(\epsilon - n^2)}{4\pi(2\epsilon+1)}\frac{\mu_0}{a^3}\cos\vartheta \quad (21)$$

V_{fast} can be obtained from eq 5. The same is true for $V_{\mathrm{fast},0}$ if we assume that in this case $\rho = \rho_0$. Putting all these terms together and integrating, we obtain the result given by eq 11.

References and Notes

(1) Lippert, E. Z. *Elektrochemistry* **1957**, *61*, 952.
(2) Ooshika, Y. *J. Phys. Soc. Jpn*. **1954**, *9*, 594.
(3) Bayliss, N. S.; McRae, E. G. *J. Phys. Chem*. **1954**, *58*, 1002.
(4) McRae, E. G. *J. Phys. Chem*. **1957**, *61*, 562.
(5) Mikkelsen, K. V.; Cesar, A.; Agren, H.; Jensen, Aa. *J. Chem. Phys*. **1995**, *103*, 9010.
(6) Aguilar, M. A.; Olivares del Valle, F. J.; Tomasi, J. *J. Chem. Phys*. **1993**, *98*, 7375.
(7) Cossi, M.; Barone, V. *J. Phys. Chem. A* **2000**, *104*, 10614.
(8) Klamt, A. *J. Phys. Chem.* **1996**, *100*, 3349.
(9) (a) Cammi, R.; Tomasi, J. *Int. J. Quantum Chem*. **1995**, *29*, 465. (b) Mennucci, B.; Cammi, R.; Tomasi, J. *J. Chem. Phys*. **1998**, *109*, 2798. (c) Cammi, R.; Mennucci, B. *J. Chem. Phys*. **1999**, *110*, 9877. (d) Capelli, C. Corni, S.; Cammi, R.; Mennucci, B.; Tomasi, J. *J. Chem. Phys*. **2000**, *113*, 11270.
(10) (a) Sánchez, M. L.; Aguilar, M. A.; Olivares del Valle, F. J. *J. Phys. Chem*. **1995**, *99*, 15758. (b) Serrano- Andrés, L.; Fülscher, M. P.; Karlström, G. *Int. J. Quantum Chem*. **1997**, *65*, 167. (c) Houjou, H.; Sakurai, M.; Inoue, Y. *J. Chem. Phys*. **1997**, *107*, 5652. (d) Li, J.; Cramer, C. J.; Truhlar, D. G. *Int. J. Quantum Chem.* **2000**, *77*, 264.
(11) Onsager, L. *J. Am. Chem. Soc*. **1936**, *58*, 1486.
(12) Brady, J. E.; Carr, P. W. *J. Phys. Chem*. **1985**, *89*, 5759.
(13) Marcus, R. A. *J. Chem. Phys*. **1956**, *24*, 966, 979.
(14) Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Phys. Chem*. **1987**, *91*, 4714.
(15) Newton, D. M.; Friedman, H. L. *J. Chem. Phys*. **1988**, *88*, 4460.